

# Simulation of Molecular ALC Spectra using Density Functional Theory

Francis Pratt  
ISIS

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Science & Technology Facilities Council

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# Requirements

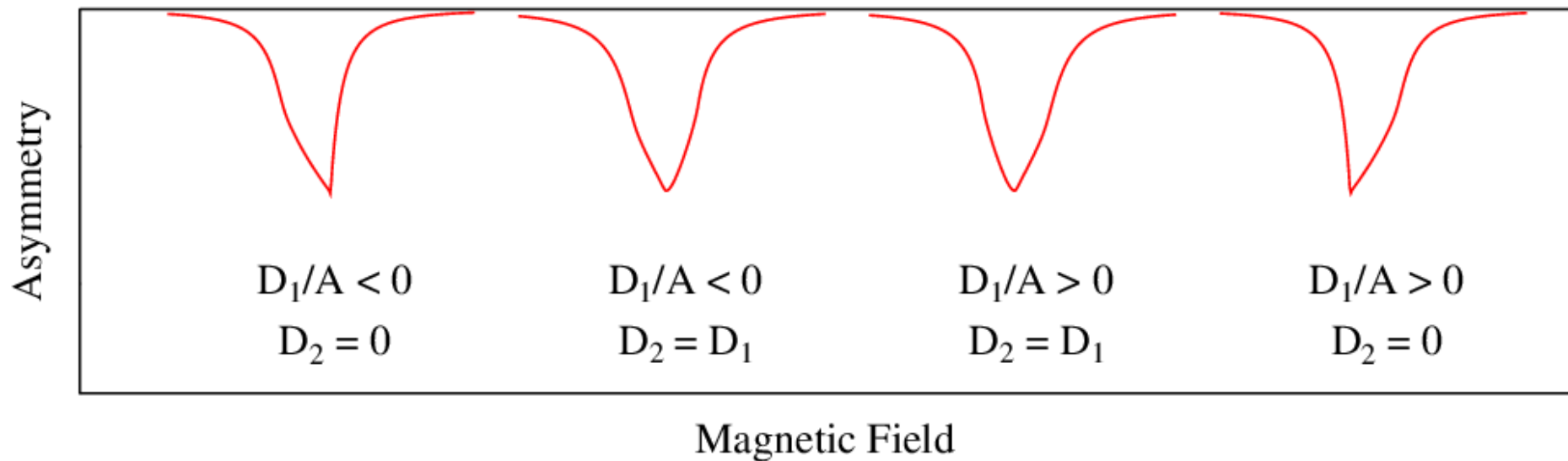
- Efficient calculation of molecular ALC spectra (establish level required for reliable results on the timescale of an ALC experiment)
- Start with low T solid state resonances (needing full hyperfine tensor)
- Aim to include zero point motion as well as thermally excited vibrations
- Validate method against well studied reference systems, e.g. TCNQ, Alq<sub>3</sub>, polymers, benzene

# Solid State ALC Resonances

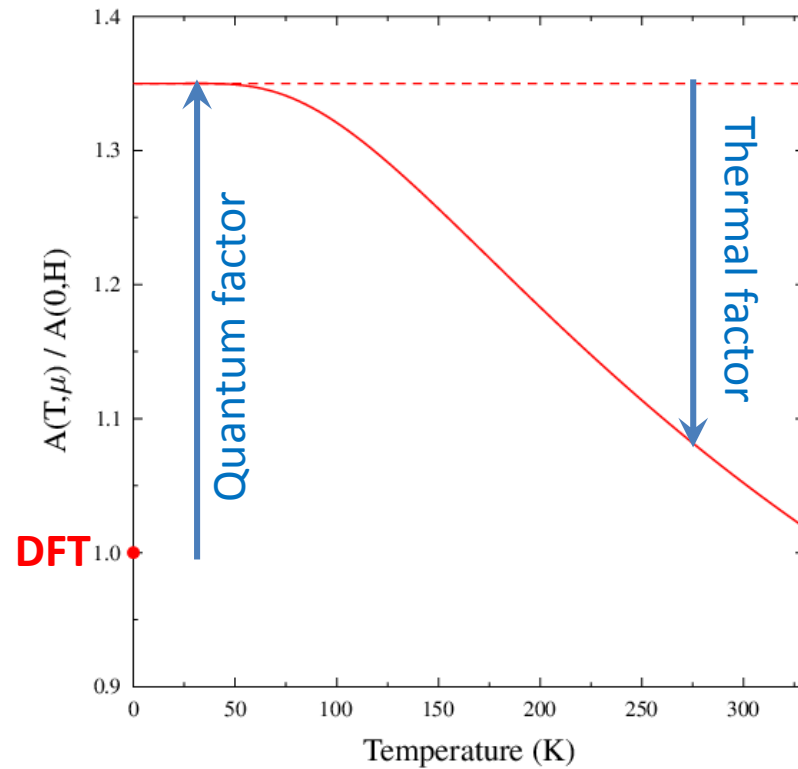
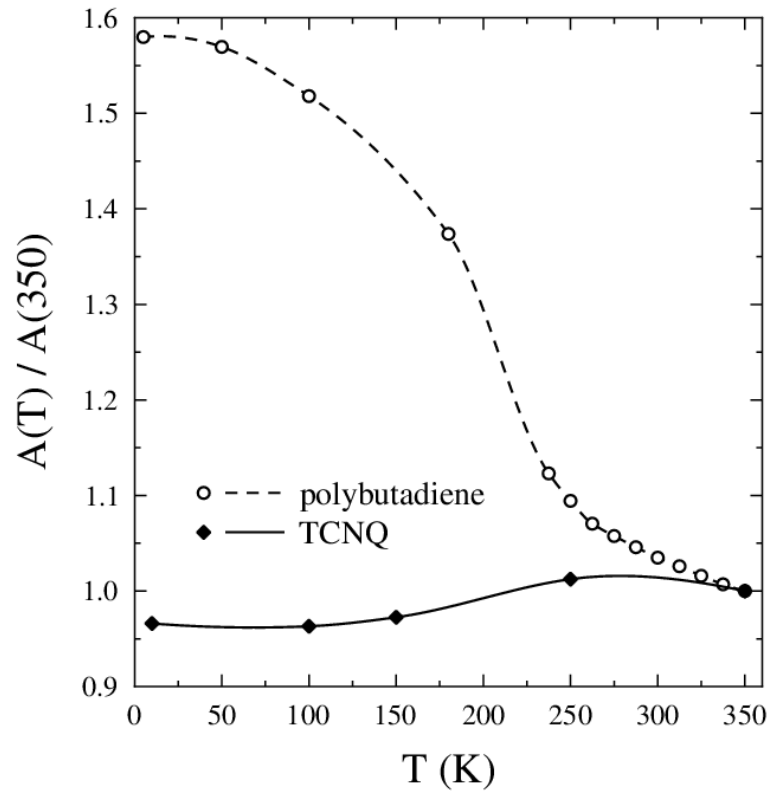
Dominated by  $\Delta_1$  resonances where the levels differ only in muon spin

Resonance position determined by the isotropic HFC parameter A

In the static low T limit the line shape is determined by the dipolar parameters  $D_1$  and  $D_2$



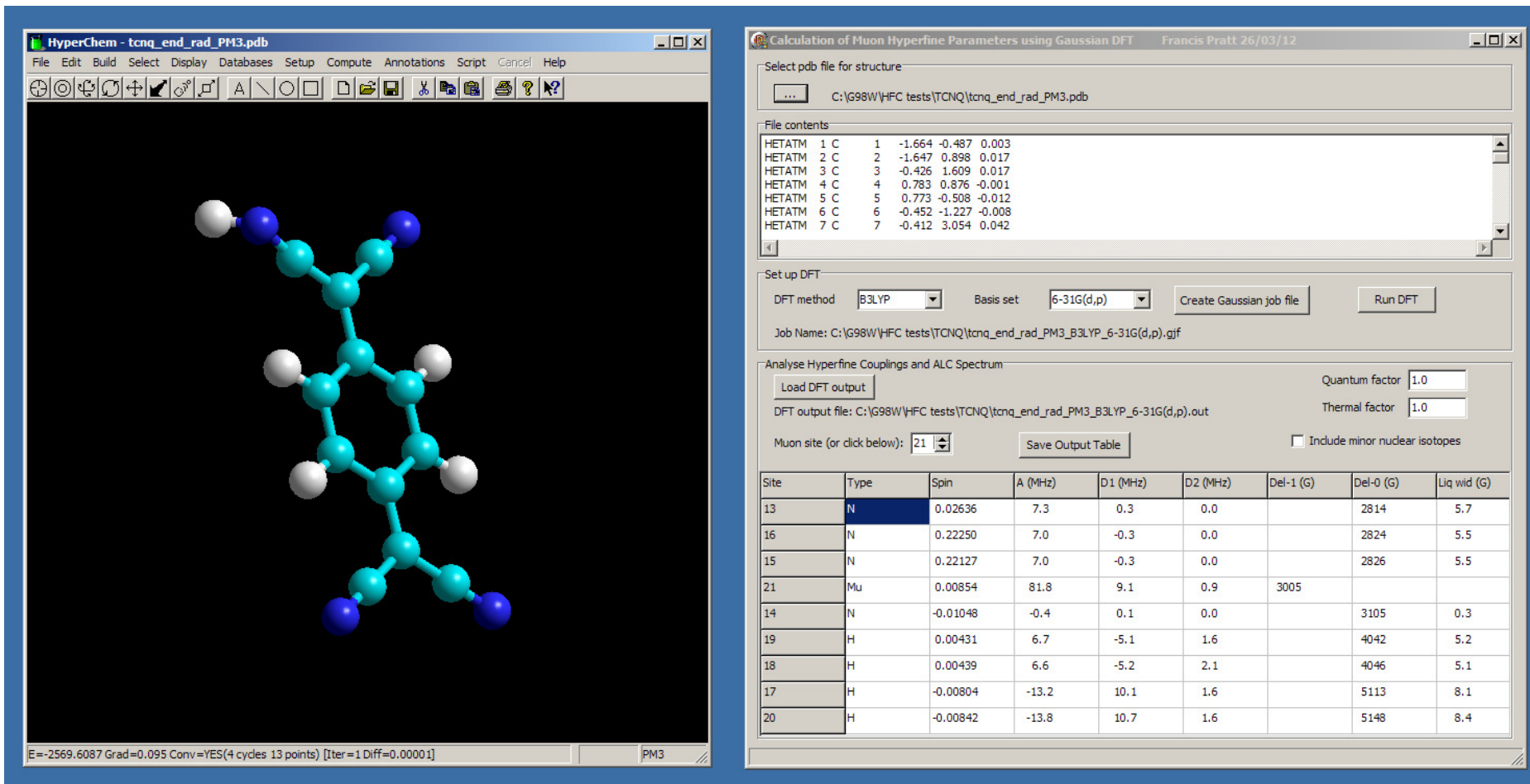
# Quantum and Thermal Effects



# MusrGaussian

- Tool for ALC spectroscopy of molecular muon radicals
- Pragmatically optimised hybrid method:
  1. Semi-empirical UHF/PM3 for relaxed radical structure
  2. Single point DFT (UB3LYP) for spin density
  3. Calculate fully anisotropic HFC tensor from DFT spin density
  4. Simulate ALC spectral lines using WiMDA/Quantum

# MusrGaussian



The image displays two software windows. The left window, titled "HyperChem - tcnq\_end\_rad\_PM3.pdb", shows a ball-and-stick model of a molecule with cyan, white, and blue atoms. The right window, titled "Calculation of Muon Hyperfine Parameters using Gaussian DFT", shows the setup for a DFT calculation and the resulting hyperfine coupling parameters.

**File contents:**

```
HETATM 1 C 1 -1.664 -0.487 0.003
HETATM 2 C 2 -1.647 0.898 0.017
HETATM 3 C 3 -0.426 1.609 0.017
HETATM 4 C 4 0.783 0.876 -0.001
HETATM 5 C 5 0.773 -0.508 -0.012
HETATM 6 C 6 -0.452 -1.227 -0.008
HETATM 7 C 7 -0.412 3.054 0.042
```

**Set up DFT:**

DFT method: B3LYP Basis set: 6-31G(d,p) Create Gaussian job file Run DFT

Job Name: C:\G98W\HFC tests\TCNQ\tcnq\_end\_rad\_PM3\_B3LYP\_6-31G(d,p).gjf

**Analyse Hyperfine Couplings and ALC Spectrum:**

Load DFT output Quantum factor: 1.0  
DFT output file: C:\G98W\HFC tests\TCNQ\tcnq\_end\_rad\_PM3\_B3LYP\_6-31G(d,p).out Thermal factor: 1.0  
Muon site (or click below): 21 Save Output Table  Include minor nuclear isotopes

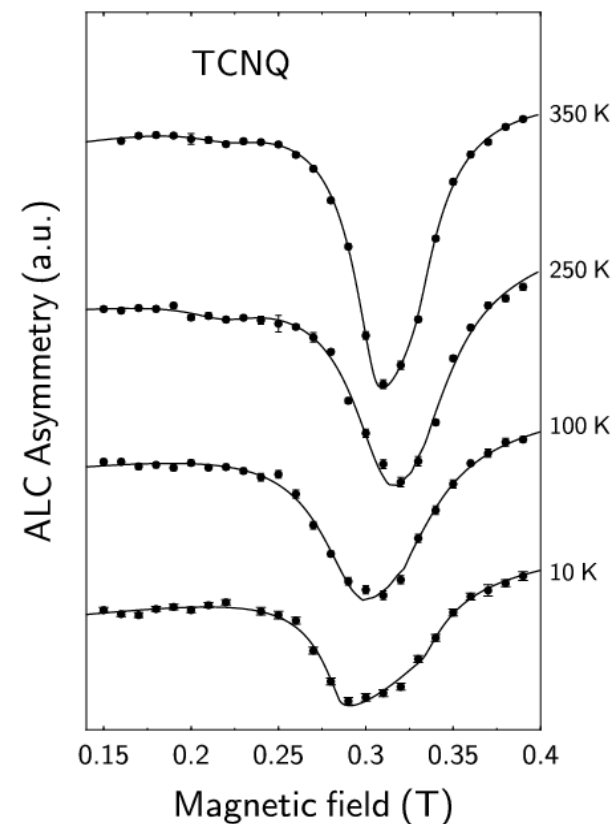
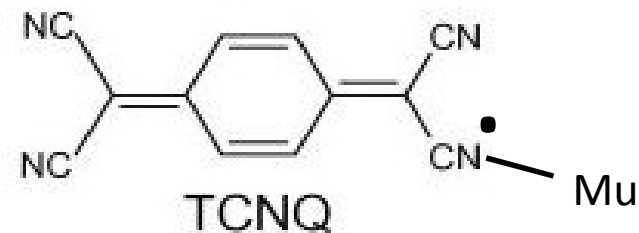
Site	Type	Spin	A (MHz)	D1 (MHz)	D2 (MHz)	Del-1 (G)	Del-0 (G)	Liq wid (G)
13	N	0.02636	7.3	0.3	0.0		2814	5.7
16	N	0.22250	7.0	-0.3	0.0		2824	5.5
15	N	0.22127	7.0	-0.3	0.0		2826	5.5
21	Mu	0.00854	81.8	9.1	0.9	3005		
14	N	-0.01048	-0.4	0.1	0.0		3105	0.3
19	H	0.00431	6.7	-5.1	1.6		4042	5.2
18	H	0.00439	6.6	-5.2	2.1		4046	5.1
17	H	-0.00804	-13.2	10.1	1.6		5113	8.1
20	H	-0.00842	-13.8	10.7	1.6		5148	8.4

E=-2569.6087 Grad=0.095 Conv=YES(4 cycles 13 points) [Iter=1 Diff=0.00001] PM3

# Optimal Calculation Level

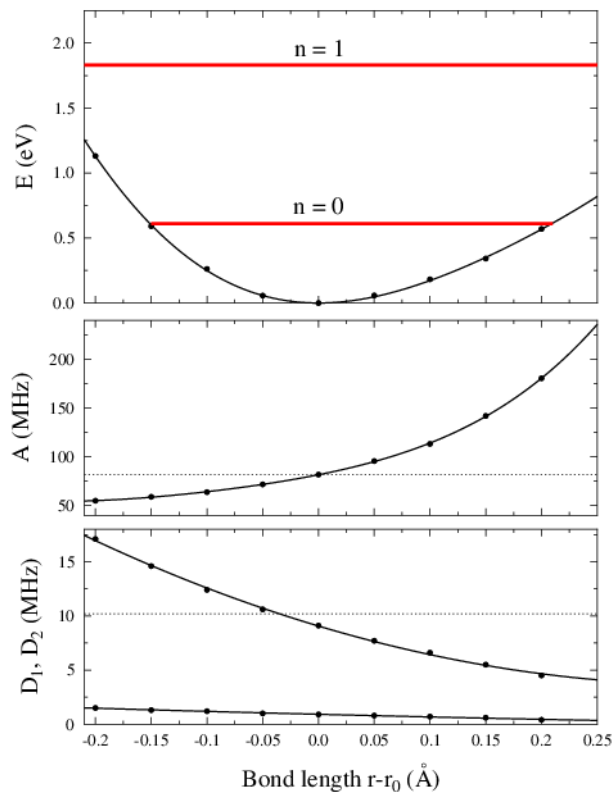
	A	D <sub>1</sub>	D <sub>2</sub>	cost
<b>Experiment (10 K)</b>	<b>82</b>	<b>10.2</b>	<b>0</b>	
STO-3G	77	10.4	0.9	14
3-21G	72	10.9	0.9	30
6-31G	88	10.0	0.9	40
6-31G(d,p)	82	9.1	0.9	120
SVP	73	9.4	0.9	149
<b>cc-pVDZ</b>	<b>75</b>	<b>9.0</b>	<b>0.9</b>	<b>177</b>
<b>(ZP corrected)</b>	<b>82.5</b>	<b>10.4</b>		
cc-pVTZ	83	8.8	0.9	2332

**Table 1** Comparison of measured hyperfine parameters in MHz for TCNQ with DFT estimates made using the B3LYP functional with progressively more costly basis sets. When the numerically calculated zero point quantum corrections of 1.10 for A and 1.15 for D<sub>1</sub> are applied, cc-pVDZ provides the best computational accuracy.



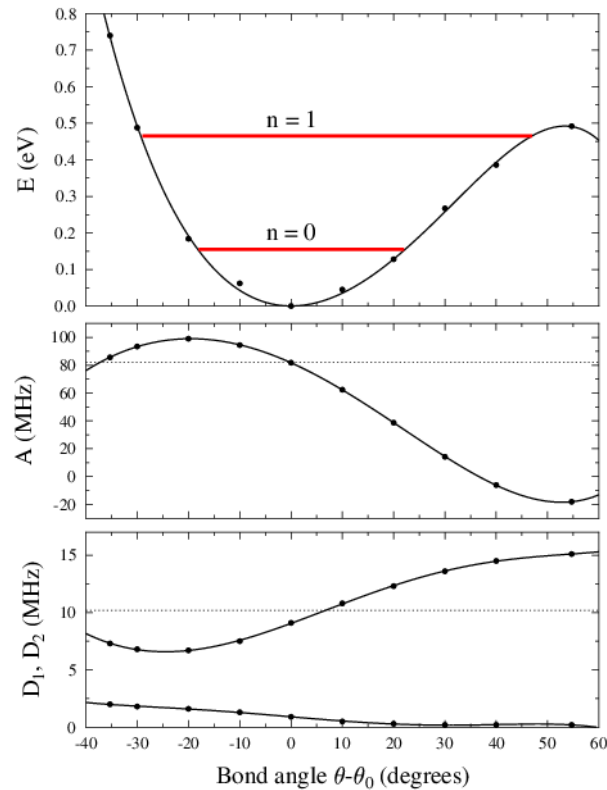
# Quantum Zero Point Corrections

## Bond Stretch



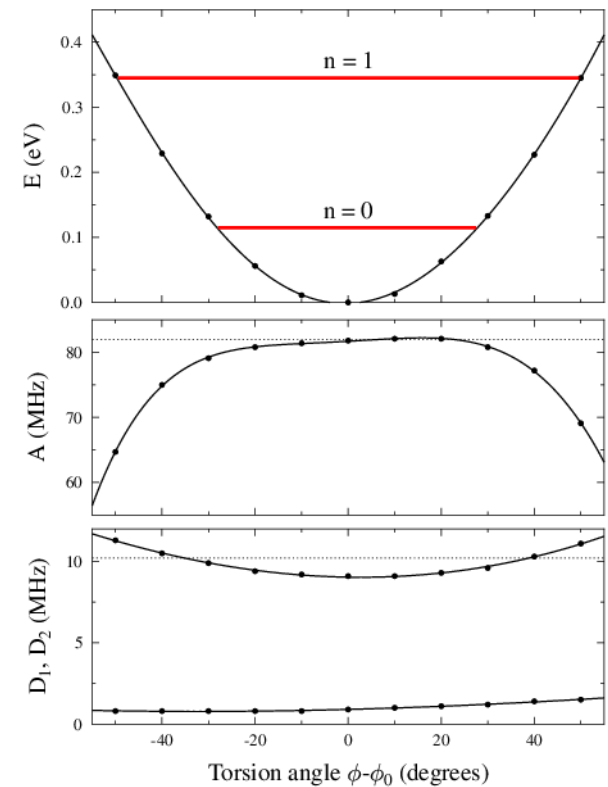
$$QF_A = 1.21$$

## Bond Bend



$$QF_A = 0.92$$

## Bond Torsion

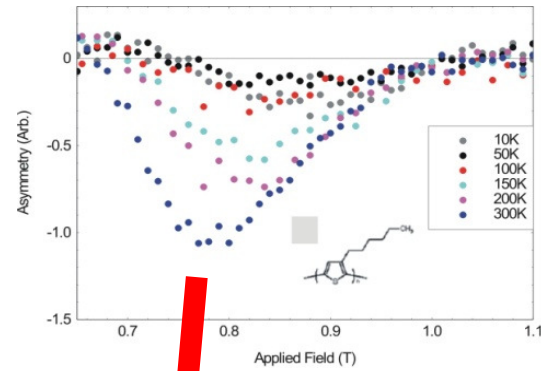


$$QF_A = 0.99$$

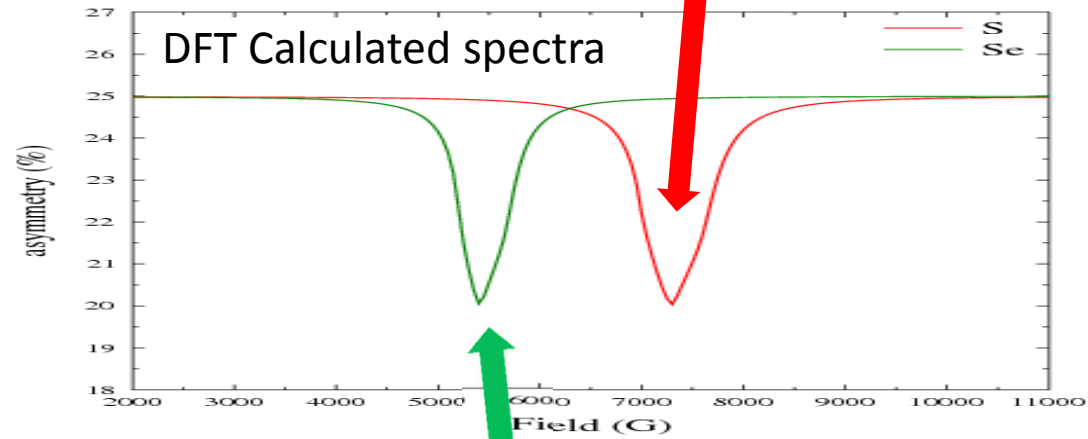
$$\text{Overall } QF_A = 1.10$$



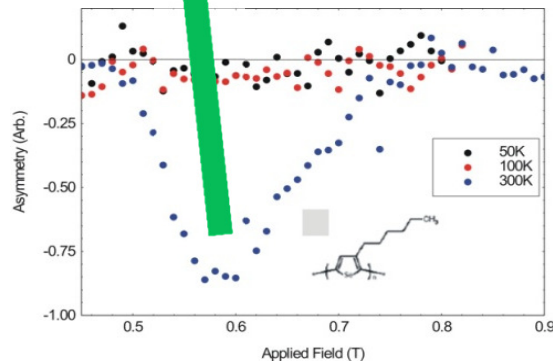
# Some Polymer Examples



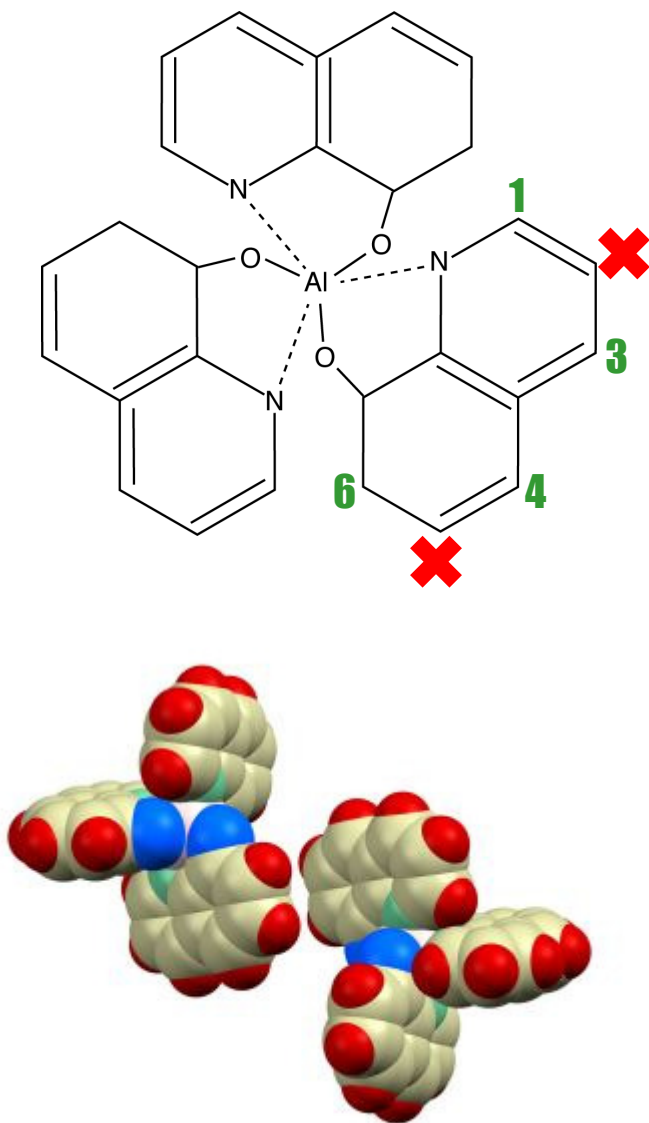
Polythiophene



Polyselenophene

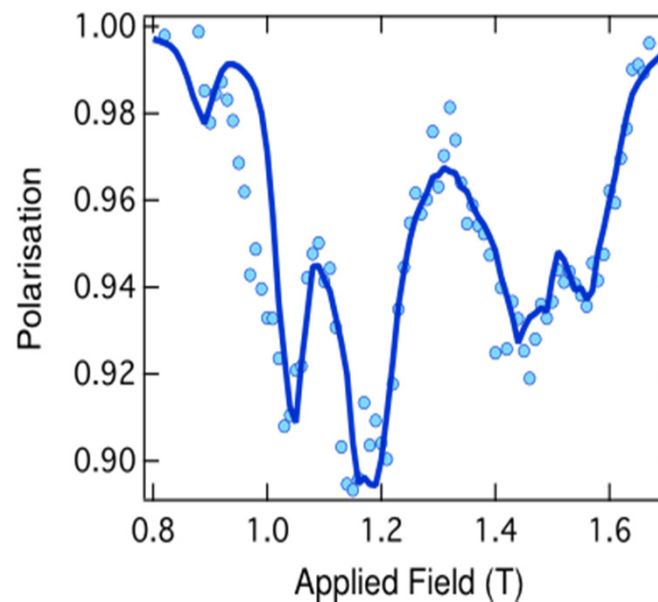


# Example of a Larger Molecule : Alq<sub>3</sub>



Full HFC tensor for 36 radicals

	Pratt						Data	
	A1	A2	B1	B2	C1	C2	Ave <sub>P</sub>	Ave <sub>dat</sub>
Site 1	427.2	416.2	449.3	411.1	420.7	393.7	419.7	420.0
Site 2	498.9	484.9	501.4	491.6	467.2	513.8	493.0	-
Site 3	380.1	381.5	405.2	357.5	374.8	323.4	370.4	386.0
Site 4	284.9	297.4	291.4	311.8	281.3	241.3	284.7	292.5
Site 5	573.2	580.5	546.7	560.3	506.0	595.0	560.3	-
Site 6	330.4	337.1	372.4	344.7	327.9	312.3	337.5	329.0



# Future Development

- Integrate ALC spectrum generation and viewing
- Links to enable use as a fit function in WIMDA/MANTID
- Move over to non-commercial code for generating the semi-empirical structure and DFT spin density
- Further work on the zero point spatial averaging effects
- Extend to thermal averaging effects in finite T

